SYNTHESIS OF HIGH-OIL ALCOHOLS BASED ON THE PHYSICOCHEMICAL PROPERTIES OF SECONDARY RAW MATERIALS OF THE ENTERPRISE "UZ-KOR GAS CHEMICAL"

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Abstract. This paper investigates the synthesis of higher fatty alcohols based on secondary raw materials of the "UZ-KOR GAS CHEMICAL" enterprise, namely low-molecular-weight polyethylene and normal paraffins. Optimal conditions of the oxidation reaction were determined, and the physicochemical properties and composition of the obtained products were evaluated using modern analytical methods. The results demonstrate the potential application of higher fatty alcohols as environmentally friendly and effective lubricity additives for diesel fuels.

Keywords: higher fatty alcohols, secondary raw materials, low-molecular-weight polyethylene, normal paraffins, oxidation process, diesel fuel, lubricating additives

Annotatsiya. Ushbu hujjatda "UZ-KOR GAS CHEMICAL" korxonasining ikkilamchi xom ashyosi, ya'ni past molekulyar og'irlikdagi polietilen va normal kerosinlar asosida yuqori yog'li spirtlar sintezi o'rganiladi.avhum. Ushbu hujjatda "UZ-KOR GAS CHEMICAL" korxonasining ikkilamchi xom ashyosi, past molekulyar og'irlikdagi polietilen va normal kerosinlar asosida yuqori yog'li spirtlar sintezi o'rganiladi. Oksidlanish reaktsiyasining maqbul shartlari aniqlandi va olingan mahsulotlarning fizik-kimyoviy xususiyatlari va tarkibi zamonaviy analitik usullar yordamida baholandi. Natijalar dizel yoqilg'isi uchun ekologik toza va samarali moylash qo'shimchalari sifatida yuqori yog'li spirtlarning potentsial qo'llanilishini ko'rsatadi.

Kalit so'zlar: yuqori yog'li spirtlar, ikkilamchi xom ashyo, past molekulyar og'irlikdagi polietilen, normal kerosinlar, oksidlanish jarayoni, dizel yoqilg'isi, moylash qo'shimchalari

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Аннотация. В данной работе исследуется синтез высших жирных спиртов на основе вторичного сырья предприятия “UZ-KOR GAS CHEMICAL”, а именно низкомолекулярного полиэтилена и обычных парафинов. Были определены оптимальные условия протекания реакции окисления, а также проведена оценка физико-химических свойств и состава полученных продуктов с использованием современных аналитических методов. Результаты демонстрируют потенциальное применение высших жирных спиртов в качестве экологически чистых и эффективных смазывающих добавок к дизельным топливам.

Ключевые слова: высшие жирные спирты, вторичное сырье, низкомолекулярный полиэтилен, нормальные парафины, процесс окисления, дизельное топливо, смазочные присадки

Введение

Today, the attention of the oil and gas industry worldwide is directed towards the development of diesel fuel production with improved environmental characteristics, containing minimal amounts of sulfur and aromatic hydrocarbons. Meeting the need for diesel fuel is associated not only with the involvement of non-traditional sources in production, but also with the use of various environmentally friendly additives. Therefore, improving the composition and quality of diesel fuels, developing and implementing technologies for obtaining additives with a new composition that enhance their operational properties remains one of the important tasks.

In the world, research is being conducted aimed at the synthesis of lubricating additives with a predetermined composition and structure, determining the mechanism of their action, and developing a technology for their production. In this regard, special attention is paid to the determination of the composition of environmentally friendly diesel fuels with improved physicochemical and operational properties, enrichment of quality and quantity indicators by additives synthesized on the basis of non-traditional raw materials, improvement and testing of technologies for the production of effective and multifunctional lubricating additives.

In our republic, special attention is paid to the development of advanced innovative technologies, the stabilization and accelerated development of industry, in particular, certain results have been achieved in the creation of technology for obtaining additives that improve the lubricating properties of diesel fuel. The New Uzbekistan Development Strategy defines important tasks for "ensuring the stability of the national economy and increasing the share of industry in the gross domestic product, widespread introduction of innovations into the economy, development of cooperative ties between industrial enterprises and scientific

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institutions." In this regard, the creation and implementation of modern technologies for obtaining effective, import-substituting, inexpensive, and environmentally friendly lubricating additives for diesel fuels based on local raw materials - paraffin and low-molecular-weight polyethylene - is of great importance.

Synthesis of HTS based on HMPE in the presence of various catalysts. 3 ml of C_{10}-C_{18} hydrocarbon fraction, 2.5 g of titanium-containing zeolite (can be increased from 0.1 to 9.5%), 36 ml of methanol or acetone solvent are added to the reactor (in a three-mouth flask), mixed in a magnetic stirrer, and thermostatized to 40-50°C (temperature maintained). After adding 1.6 ml of a 35% hydrogen peroxide solution, the duration of the experiment was determined (Fig. 1).

With an increase in the molar ratio of hydrocarbons and hydrogen peroxide from 1:1 to 13:1 and the catalyst concentration (up to 70 g/l), the yield of HTS increases. The completion of the experiment is determined by gas-liquid chromatography to determine the HTS content in the reaction mixture. After the completion of the oxidation reaction, the reaction mixture is sent for separation.

During the distillation of the reaction mixture from the rectification column (10 theoretical plates), the solvent methanol is released, while in the cubic residue, a HTS solution (45%) in the hydrocarbon fraction is released. When the resulting cubic residue is distilled in a vacuum (column with 5 theoretical plates), the hydrocarbon fraction accumulates in the distillate, leaving HTS in the cubic residue.

Its composition is as follows: C_{10}-17,05%, C_{11}-29,94%, C_{12}-34,74%, C_{13}-7,51%, C_{15}-7,51%, C_{16}-3,95%, C_{17}-2,73%, C_{18}-1,89% containing alcohols. The degree of HTS separation from the reaction mixture is 99.5-99.6%.

Method for obtaining higher fatty alcohols by oxidation of normal paraffin hydrocarbons. 25-50 g of paraffin is placed in a round flask with a volume of 100 ml and 1.25-2.5 g of boric acid is added to it. The temperature of the reaction mixture is increased to 165°C, then a stream of air and nitrogen is introduced, which is controlled by a rheometer. The consumption of oxidizing gas per 1 kg of paraffin is maintained at 70 l/hour.

The mixture of oxidizing gases, passing through a calcium chloride dryer, enters the reactor, and the excess unreacted gas mixture is discharged from the reactor into the atmosphere through a reverse cooler.

In the refrigerator, the condensed paraffin vapor droplets are returned to the reactor and collected in the resulting water trap. The oxidation process of paraffin takes 4 hours, and 4-6 g of the oxidized sample is analyzed every hour to determine the amount of hydroxyl groups. During the experiment, temperature, air content, and nitrogen are monitored. During the experiment, the system is monitored. The

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results of the observation are recorded.

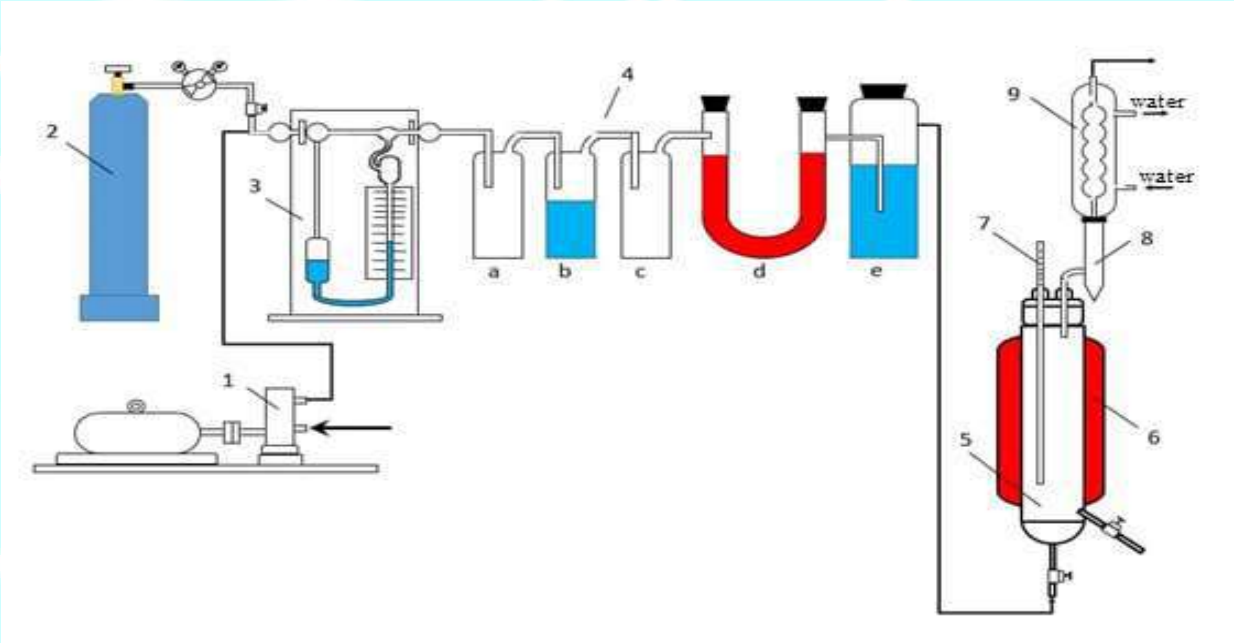


Figure 1. Diagram of a laboratory installation for obtaining higher fatty alcohols by oxidation of normal paraffinic hydrocarbons:

1-air sprayer, 2-nitrogen tank, 3-rheometer, 4-$CaCl_2$ dryer, 5-reactor, 6-heater, 7-thermometer, 8-Din-Stark apparatus, 9-reverse cooler.

As paraffins, a control experiment is conducted by oxidizing cetane, one of the high-molecular hydrocarbons, as a standard. In this case, the yield of the primary alcohol is calculated by the amount of hydroxyl groups. The samples taken to determine the hydroxyl group content are placed in a 25 ml conical flask and the sample is repeatedly soaped with distilled water in a 1:1 ratio.

Water is added to the sample in the flask, stirred for several minutes, and then placed in a hot water bath. After this, the lower water layer is separated with a pipette, and hydrolysis is repeated.

It is easy to determine the completion of hydrolysis by visual observation; if the saponification proceeds well, the water will be clear (usually washed 3-5 times with distilled water).

After hydrolysis, the product is dried; to determine the hydroxyl group number, it must be dry. For this, oxide is dissolved in ether (1:1) and dried on sodium sulfate.

After drying, the product is transferred to another flask for decantation, the ether is distilled, and the oxidant is analyzed. Due to the small number of hydroxyl groups in high-molecular-weight alcohols, saponification and drying of the oxidant should be carried out with caution, since insufficient hydrolysis and the presence of moisture in the sample lead to errors in determining the results.

Determination of hydroxyl number. After the oxidation process is complete, higher fatty alcohols can be separated into fractions, which is carried out

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as follows: the oxidant and free boric acid residues are separated by filtration, after which unreacted hydrocarbons are distilled from them under vacuum (usually the difference in boiling points between hydrocarbons and boric acid esters of such hydrocarbons exceeds 100°C).

After treating the product formed as a result of oxidation with an aqueous solution of alkali, a small amount of acids is retained in them, and the unreacted hydrocarbons are returned to the oxidation reactor. The residue mainly contains boric acid esters, which, upon freezing at room temperature, turn into a uniform dark yellow mass. Boric acid esters are placed in a flask for hydrolysis. Hydrolysis is carried out at a temperature of 95-98°C and intensified. The reaction proceeds according to the equation:

$$(RO)_3B + 3H_2O \rightarrow 3ROH + H_3BO_3$$

After hydrolysis of borate alcoholates, the alcohols are separated from the water, distilled under residual pressure of 3-5 mm Hg, and the amount of hydroxyl groups (in %) and molecular mass of the alcohols are determined.

Determination of the hydroxyl number by the Verley method. Two samples of the synthesized oxide (0.1-0.2 g) are placed in conical flasks and sealed with stoppers, then 10-15 ml of the mixture (depending on the approximate composition of hydroxyl groups) is poured into each flask, 12 mass parts of acetic anhydride and carefully dehydrated 88 mass parts of distilled pure pyridine are added. At the same time, a control experiment is conducted. A sample with a flask mounted on bent forks is heated in a water bath at 60°C for 0.5-2.0 hours.

After the mixture cools, an equal amount of distilled water is poured into three flasks, and the resulting acetic acid is titrated with a 0.5 N NaOH solution in the presence of phenolphthalein. Acetic anhydride reacts with the hydroxyl groups of alcohol according to the following scheme:



The isolated acetic acid forms a salt with pyridine, which is stable in an anhydrous medium and decomposes quickly with the addition of water. This prevents the hydrolysis of the ester formed by binding the acid through pyridine.
The proportion of hydroxyl groups is calculated using the formula:

$$x = \frac{(b-a)\cdot 0.0085}{d}\cdot 100$$

Here: α-amount of 0.5n NaOH solution used for titration in the control experiment, ml;

b-amount of 0.5 NaOH solution used for sample titration, ml;

coefficient expressing the weight number (in g) of hydroxyl groups corresponding to 0.0085-1 ml of 0.5 n NaOH solution;

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d - mass of oxide or alcohol, g.

From the results obtained three times, the average number of hydroxyl groups is calculated.

Determination of the yield of alcohols. Theoretically, the number of hydroxyl groups in cetyl alcohol is equal to 242 molecules.

$$17 \cdot 100/242 = 7{,}03\%$$

Also, alcohol is formed during oxidation:

$$3{,}1 \cdot 100/7{,}03 = 44{,}1\%$$

A material balance of the process is compiled (Table 1).

Table 1

Cetane oxidation material balance

Received			Accepted		
Raw material	g	%	Raw material	g	%
Cetane	50	100	Reduced cetane	33	66
			Oxidized alcohols	17	34
Total	50	100	Total	50	100

Table 2

Determining molecular weight:

Number of generated	Values, g
Alcohol content	0,3115
Δт, □C	0,39
k	5,12
Benzene content	17,2
Identified	M = 238
Calculated	M = 242
Content of hydroxyl groups	(%)
Alcohol content,	0,3042
Amount detected:	OH = 6,85
Calculated: Amount	OH = 7,03

The mass of all oxidant samples was 15 g. As a result of vacuum distillation of 43.5 g of saponified oxide, 25.5 g of cetane and 17.5 g of alcohol were separated into components.

This article presents methods for purifying and determining the physicochemical properties of starting materials used in the synthesis of higher fatty alcohols. Including: optimal conditions for the synthesis of HTS based on HDPE and paraffin have been determined. Modern physicochemical methods for determining the structure and quantity of HTS and determining the lubricating properties of diesel fuel are presented.

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